PAPER

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Static and time-resolved mid-infrared spectroscopy of $Hg_{0.95}Cd_{0.05}Cr_2Se_4$ spinel

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Abstract

Static and time-resolved mid-infrared spectroscopy of ferromagnetic single crystal $Hg_{0.95}Cd_{0.05}Cr_2Se_4$ was performed below the absorption edge, in order to reveal the origin of the electronic transitions contributing to the magneto-optical properties of this material. The mid-infrared spectroscopy reveals a strong absorption peak around 0.236 eV which formerly was assigned to a transition within the selenide–chromium complexes (ν_{Se}–Cr^{2+}). To reveal the sensitivity of the transition to the magnetic order, we performed the studies in a temperature range across the Curie temperature and magnetic fields across the value at which the saturation of ferromagnetic magnetization occurs. Despite the fact that the Curie temperature of this ferromagnetic semiconductor is around 107 K, the intensity of the mid-infrared transition reduces substantially increasing the temperature, so that already at 70 K the absorption peak is hardly visible. Such a dramatic decrease of the oscillator strength is observed simultaneously with the strong red-shift of the absorption edge in the magnetic semiconductor. Employing a time-resolved pump-and-probe technique enabled us to determine the lifetime of the electrons in the excited state of this optical transition. In the temperature range from 7 K to 80 K, the lifetime changes from 3 ps to 6 ps. This behavior agrees with the phenomenon of giant oscillator strength described earlier for weakly bound excitons in nonmagnetic semiconductors.

Keywords: magnetic semoconductors, mid-infrared spectroscopy, time-resolved measurements, Fourier transform infrared spectroscopy

(Some figures may appear in colour only in the online journal)

1. Introduction

Ferromagnetic semiconductors are often mentioned among promising candidates for future spintronic applications [1–5] due to the fact that the response of electric charges to electric fields in these materials is strongly correlated with the magnetic state of the latter [6]. Optical control of magnetism in such semiconductors is also often predicted to be effective [7]. One of the ultimate goals of the rapidly developing area of photo-induced phase transitions [8] is to find a spectrally narrow electronic excitation a selective pumping of which is able to launch dramatic magnetic changes and hopefully switch the medium into another metastable state without an increase of the kinetic energy of electrons and entropy. Therefore, finding an electronic excitation with the spectral features of excitons and a strong coupling to the magnetic order can be a solution for the problem of the huge heat dissipations in nowadays magnetic recording technology.

A giant effect of magnetic field and temperature on the optical transmissivity of magnetic semiconductors in the proximity of a magnetic phase transition, is one of the manifestations of the spin-charge correlations. In particular, unlike classical semiconductors, the correlations result in a substantial red-shift of the absorption edge and giant magnetorefractive effect in the infrared range [9].

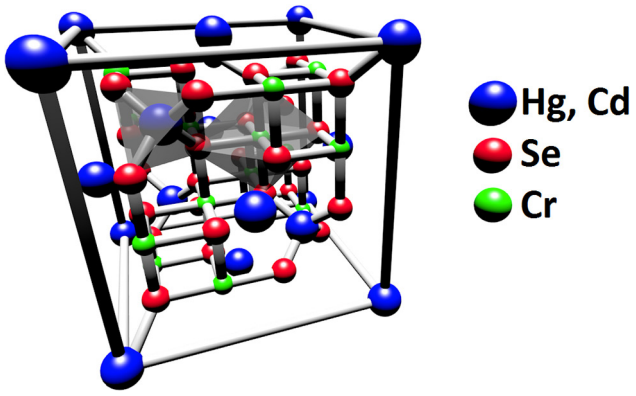

Figure 1. Crystal structure of ACr_2X_4 spinel with CrX_6 octahedron and AX_3 tetrahedron.

$HgCr_2Se_4$ (a chromium-chalcogenide spinel) is a well-known ferromagnetic semiconductor. It is a convenient model system for fundamental spectroscopy and spintronic studies due to its large magnetoresistance and magneto-optical effects [9–13]. In particular, recent studies of absorption of non-polarized infrared radiation in (Hg, Cd)Cr_2Se_4 crystals revealed several mechanisms responsible for the magnetotransmission (magnetoabsorption) and magnetoreflection of light [14–16]. Rather strong spectral lines just below the absorption edge have been reported in these semiconductors. However, the coupling of these features to magnetism, their temperature and magnetic field dependencies as well as their ultrafast dynamics have not been clarified until now.

Here we report the results of mid-infrared static and time-resolved spectroscopy measurements of the ferromagnetic semiconductor $Hg_{0.95}Cd_{0.05}Cr_2Se_4$ below the absorption edge. We pay particular attention to the dependence of the absorption spectrum on magnetic field and temperature. With the help of a time-resolved pump-probe technique we estimate the lifetime of the electrons in the excited state. The observed dependencies of the absorption spectrum and the lifetime on magnetic field and temperature qualitatively agree with the behavior expected for a weakly bound exciton coupled to the magnetic order [17, 18].

The paper is organized as follows. In section 2 we provide a description of the studied sample and employed experimental techniques. In sections 3 and 4, we describe the absorption spectra with and without an external magnetic field respectively. In section 5, we report the results of time-resolved measurements. The findings and conclusions of this paper are then summarized in section 6.

2. Sample and experimental technique

A cubic ferromagnetic spinel belongs to the space group $Fd3m(O_h^7)$ with a general formula AB_2X_4, where A is a divalent non-magnetic cation (e.g. Cd or Hg) and X is a divalent anion (e.g. Se or S). The bonding between A and X is tetrahedral, but the bonding between B (e.g. Cr) and X is octahedral or pyramidal (see figure 1). The exchange interaction depends

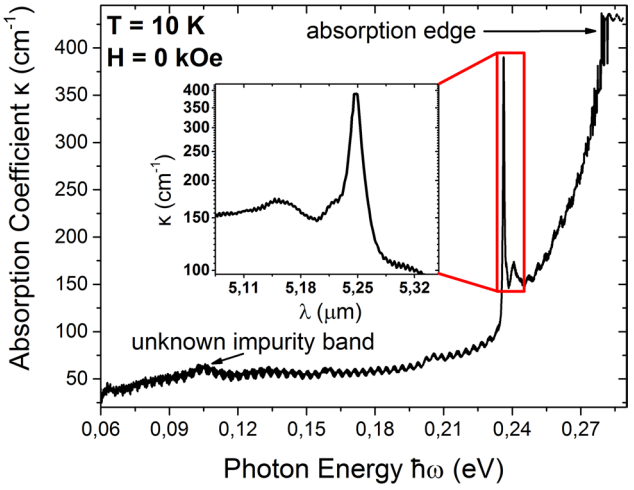

Figure 2. The absorption spectrum $\kappa(\hbar\omega)$ of $Hg_{0.95}Cd_{0.05}Cr_2Se_4$ crystal at 10 K and without magnetic field ($\boldsymbol{H} = 0$ kOe). The inset enlarges the spectral features around $\hbar\omega = 0.236$ eV.

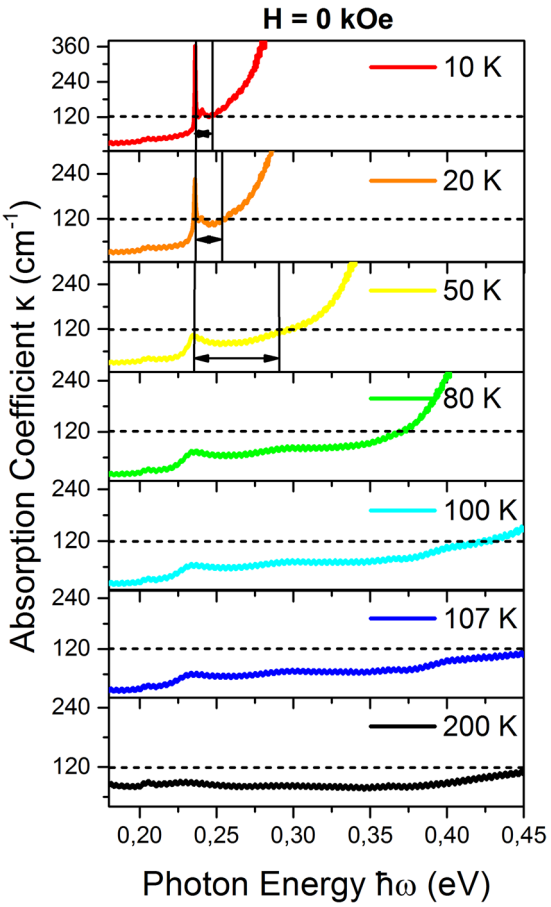

Figure 3. Absorption coefficient versus the photon energy $\hbar\omega$ for $Hg_{0.95}Cd_{0.05}Cr_2Se_4$ crystal. The pronounced peak at 0.236 eV disappears upon increasing the temperature. Simultaneously, the absorption edge shifts to higher energies upon a temperature increase due to a decrease of the exchange splitting of the conduction and the valence bands [12, 22, 24, 28, 29]. The arrows indicate the separation energy ε between the peak at 0.236 eV and the absorption edge. The latter is defined as the energy at which the interband absorption exceeds 120 cm^{-1} (see dashed line).

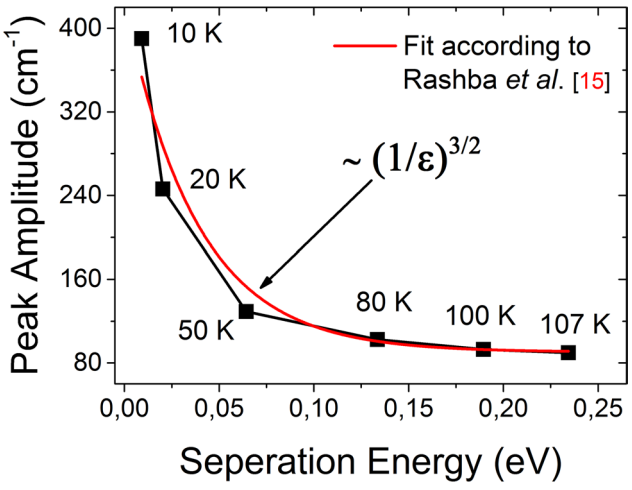

Figure 4. Peak amplitude at 0.236 eV as a function of the separation energy ε, which is defined as the energy difference between the peak at 0.236 eV and the absorption edge. The latter is defined as the energy at which the interband absorption exceeds 120 cm^{-1} (see dashed black line figure 3). The solid line is fit using $(1/\varepsilon)^{3/2}$-law. The behavior is qualitatively similar to the one of giant oscillator strength for weakly bound excitons [17, 18].

on the distance between the chromium ions (Cr^{3+}) and is dominated by the superexchange mechanism. According to the Goodenough-Kanamori-Anderson rules the interaction is ferromagnetic due to the orthogonality (90°) of the Cr^{3+}–Se^{2-}–Cr^{3+} bonds. A direct overlap of the wavefunctions of the electrons of the Cr^{3+} ions favors an antiferromagnetic exchange coupling [19, 20].

The chromium-chalcogenide spinel $HgCr_2Se_4$ is usually a p-type magnetic semiconductor with the density of holes $n \approx 10^{19}$ cm^{-3} and a relatively high mobility of electrons up to ~10^3 cm^2 V^{-1} s^{-1} [21]. The effective mass of the electrons is $m^* = 0.3\ m_0$ at 300 K and $m^* = 0.15\ m_0$ at 4 K [12, 22, 23], where m_0 is the free electron rest mass. The optical properties of $HgCr_2Se_4$ are similar to those of direct band gap semiconductors. The band gap of $HgCr_2Se_4$ decreases from $E_g = 0.84$ eV at room temperature (RT) to 0.26 eV at 4.2 K [12, 22, 24, 25]. This is of the same order in comparison with the band gap in pure $CdCr_2Se_4$ (1.3 eV at RT) [26] and $HgGa_2Se_4$ (1.93 eV at RT) [27]. The origin of electronic levels and optical transitions in (Hg, Cd)Cr_2Se_4 was discussed in [22, 24, 28–32]. $HgCr_2Se_4$ and $CdCr_2Se_4$ have distinctly different electronic structures [22, 24, 28, 29] and further Cd doping does lead to an almost linear increase of the Curie temperature up to 130 K for $CdCr_2Se_4$ spinel.

The single crystals studied here were grown with the help of the chemical transport reaction technique using $CrCl_3$ as a carrier agent. The data discussed in this paper were obtained for the sample cut from a $Hg_{0.95}Cd_{0.05}Cr_2Se_4$ single crystal perpendicular to the [1 0 0] crystallographic axis, in a form of a square plate 3×3 mm^2 with the thickness $d = 0.14$ mm. Magnetometry measurements show that the Curie temperature of the crystal is approximately $T_C \approx 110$ K (at $H = 5$ kOe). The magnetization is saturated at the field of 0.5 kOe.

Absorption measurements were performed in the range 4000–350 cm^{-1} (0.5–0.04 eV) with a Bruker Vertex Fourier

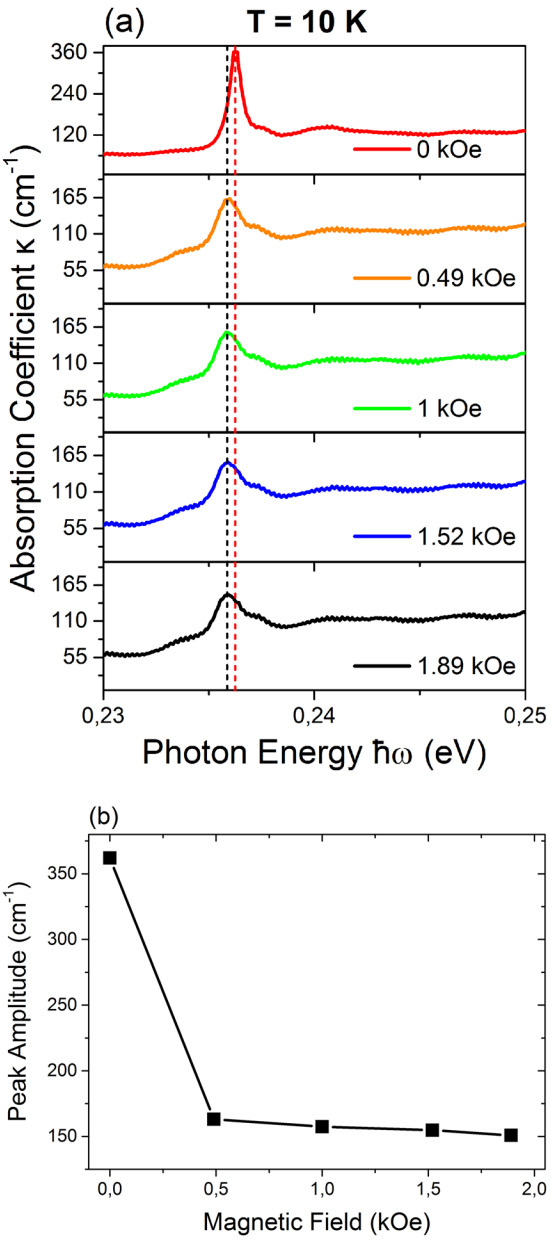

Figure 5. (a) Magnetic field dependence of the absorption of $Hg_{0.95}Cd_{0.05}Cr_2Se_4$ crystal below the band gap measured at $T = 10$ K. Both dashed lines (red, black) indicate positions of the peak with and without magnetic field. (b) Absorption measured at 0.236 eV as a function of the magnetic field.

transform infrared (FTIR) spectrometer. The spectral resolution was 1 cm^{-1}. The measurements were performed at normal incidence. A custom-made magnet was designed and built into this FTIR spectrometer allowing a magnetic field up to approximately 2 kOe to be applied vertically in the plane of the sample. Time-resolved measurements were performed with the help of the free electron laser for infrared experiments (FELIX) facility in Nijmegen (The Netherlands). In the pump-probe experiments, we measured the changes in transmissivity of the sample induced by mid-infrared pumping as a function of time. The measurements were performed with the pump and probe beams having the same central photon energy (around 0.236 eV). Both beams consisted of macropulses with

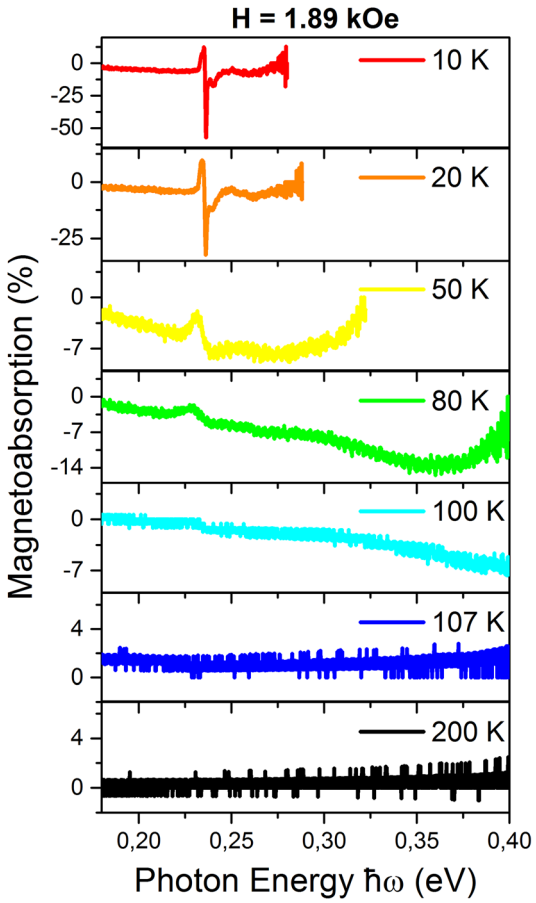

Figure 6. Magnetoabsorption of $Hg_{0.95}Cd_{0.05}Cr_2Se_4$ crystal as a function of the photon energy $\hbar\omega$, at different temperatures as indicated.

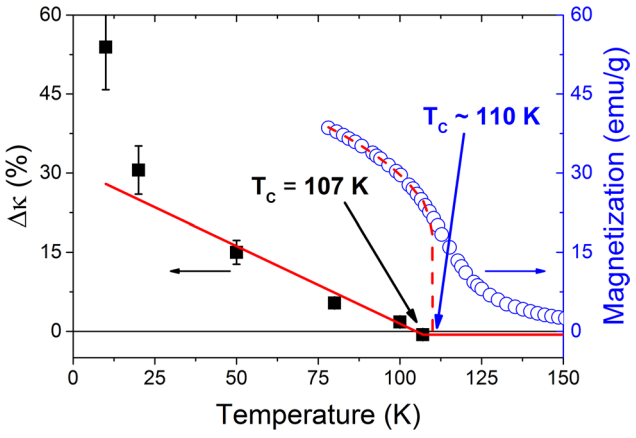

Figure 7. The temperature dependence of the magnetoabsorption (squares) at $\hbar\omega = 0.236$ eV and H = 0.5 kOe. The Curie temperature is estimated to be $T_C = 107$ K. This is in very good agreement with the Curie temperature estimated from magnetometer measurements (blue circles) in the field of 5 kOe. The data were fitted by function $M = M_0\left(1 - \frac{T_C}{T}\right)^{1/2}$ (dashed red line), where M_0 and T_C are fit parameters.

duration about 8 μs and the repetition rate of 5 Hz. Each macropulse contained a train of micropules with duration of 1 ps and the repetition rate of 25 MHz. Each micropulse was split into two parts with the help of a beam splitter. The

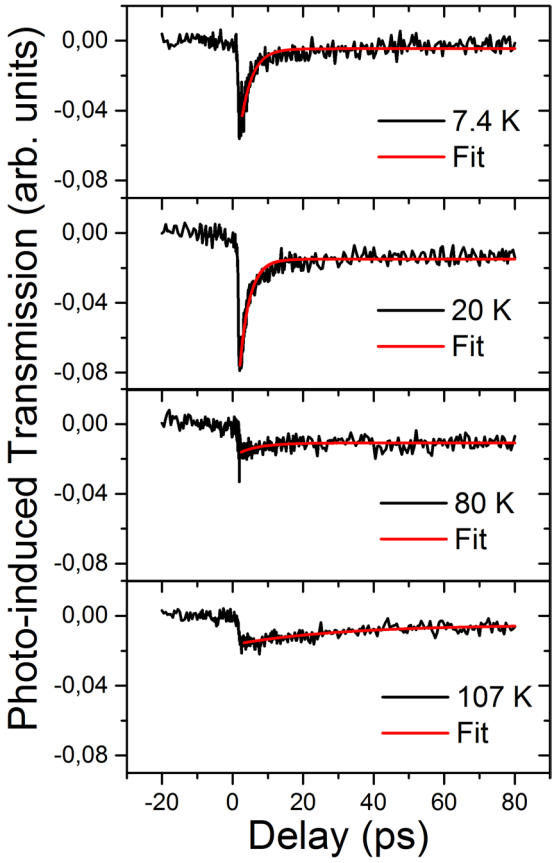

Figure 8. Dynamics of the photo-induced transmission measured using a pump-probe technique for the central photon energies of the pump and probe pulses at $\hbar\omega = 0.236$ eV.

most intense part was used as a pump and the less intense as a probe. The time delay between the pump and pulses was set with the help of a mechanical delay stage. The beams were nearly at normal incidence at an angle less than 10° with respect to the sample normal. Both beams were focused into spots approximately 200 μm in diameter. The fluence of the pump pulse was 1.9 mJ cm^{-2} and the fluence of the probe was at least 10 times lower. The detection in the experiment relied on a balanced-detection acquisition scheme. It involved a reference beam, with the same central photon energy, time structure and intensity as the probe beam, undergoing the same optical path as the probe itself, but with pulses delayed by 20 ns [33]. In the measurements, there was a possibility to apply a horizontal magnetic field in the sample plane and change the temperature across the sample from 6 K to 300 K.

3. Absorption spectroscopy

The absorption spectrum of $Hg_{0.95}Cd_{0.05}Cr_2Se_4$ crystal measured without external magnetic field ($\boldsymbol{H} = 0$ kOe) is shown for the range just below the absorption edge at a temperature of 10 K (figure 2).

The absorption coefficient κ was calculated according to [14, 23] as $\kappa = \frac{1}{d}\ln\left(\frac{(1-R)^2}{T}\right)$, where R and T refer to the reflection and transmission coefficients, and d is the sample thickness ($d = 0.14$ mm). The reflection coefficient

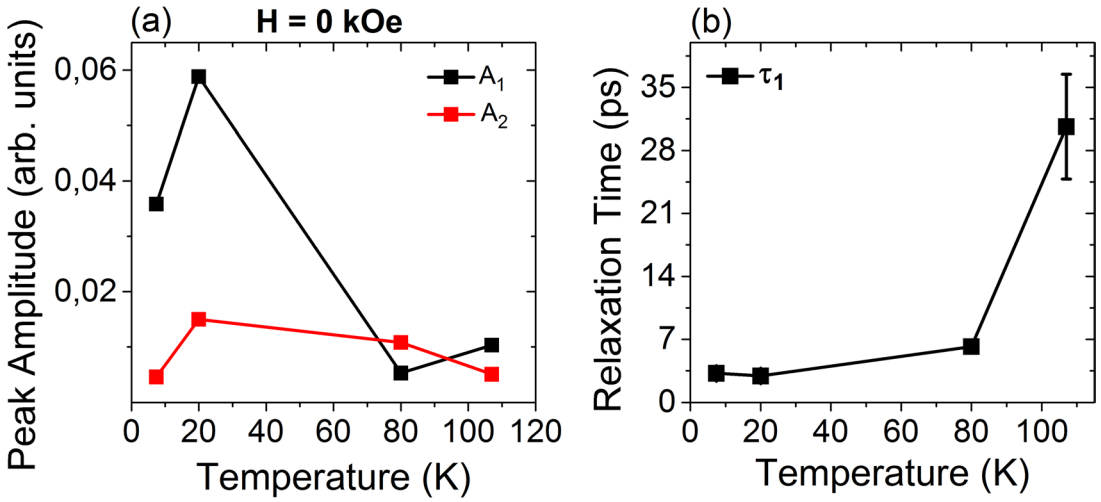

Figure 9. The results of the fit of the time dependencies shown in figure 8. (a) Temperature behavior of the amplitudes A_1 and A_2. (b) Relaxation time τ_1 as a function of temperature.

in this spectral range was assumed to be constant ($R = 0.3$), according to [15, 34].

The band gap energy is found to be around 0.28 eV which is in good agreement with the previous reports [12, 22, 24, 29]. Below the absorption edge several lines can be distinguished. The most pronounced one is at 0.236 eV (5.26 μm)—earlier, this had been assigned to a peak of the doublet formed by the intercenter transition within the selenide vacancies and chromium complexes (ν_{Se}–Cr^{2+}) with an electron bound to it (see inset of figure 2). Note that earlier the signatures of the transition were studied in pure $HgCr_2Se_4$ and $CdCr_2Se_4$ spinels [14, 22]. The absorption spectra are similar to those reported previously [14, 22]. Each selenium vacancy ν_{Se} provides two electrons. These electrons will be either excited to the conduction band or confined between three nearest-neighbor chromium ions in an octahedral site [35]. The level of vacancies in the Se sublattice is around 0.1–0.15 ($Se_{3.85–3.9}$) that is typical value for such kind of materials [14, 15]. The small peaks at 0.2 eV and 0.16 eV can be related to vacancy transitions from the valance band (E_V-4p Se) to the acceptor band (ν_{Hg}) [22]. In the region below 0.16 eV tails of multiple phonon absorptions are seen [34, 36].

In the following we focus on the most pronounced absorption peak in the spectrum of the spinel at 0.236 eV. Figure 3 shows how the absorption depends on temperature in the range from 10 K to 200 K.

In figure 4 we see that the peak amplitude of the transition at 0.236 eV decreases upon a temperature increase. As this decrease in amplitude also occurs simultaneously with a shift of the absorption edge, the behavior is qualitatively similar to the one expected for weak-bound excitons as described by Rashba and Gurgenishvili (1962) in [17]. Note, that the lifetime of the excited state of this exciton must be inversely proportional to the giant oscillator strength [18]. According to [37], Se vacancies are predominant among possible defects in $Hg_{1-x}Cd_xCr_2Se_4$. Due to the anion vacancies the crystal contains many Cr^{2+} ions which in combination with selenide vacancy form (ν_{Se}–Cr^{2+}) complexes. The complexes can play the role of magnetic-order-sensitive trapping centers [38]. At low temperatures these effective trapping centers can efficiently attract excitons (electron–hole pairs) [39].

4. Magnetoabsorption spectroscopy

Figure 5 shows the absorption spectra of the spinel measured at $T = 10$ K for different magnetic fields. It is seen that upon increasing of the strength of the magnetic field the amplitude of the absorption peak decreases significantly. Moreover, the peak around 0.236 eV shifts slightly to lower energies with an increase of the magnetic field up to 0.5 kOe (see figures 5(a) (dashed lines) and (b)) [40].

To emphasize the effect of the field, we determined the magnetoabsorption spectra (see figure 6) defined as the relative change of the absorption coefficient κ for unpolarized light with ($\kappa(H)$) and without ($\kappa(0)$) the external magnetic field, respectively $\Delta\kappa = \frac{\kappa(H)-\kappa(0)}{\kappa(0)} \cdot 100\%$ [12, 16].

From the shape of the magnetoabsortpion spectrum in figure 5 it is seen that the energy of the transition around 0.236 eV experiences a shift to lower energies upon the application of an external magnetic field.

Such a dependence of the absorption peak on the applied magnetic field does not necessarily imply that the effect is sensitive to the magnetic order. We note that if the magnetoabsorption is sensitive to the magnetic order, the complex coefficient of refraction $\tilde{n} = n + i\kappa$ must be a function of the net magnetization. According to the Onsager principle the Taylor series of the complex refraction coefficient can contain only even terms with respect to the magnetization $\tilde{n} = n(0) + aM^2 + bM^4 + \ldots$. According to the Landau theory of phase transitions $M^2 = M_0\left(1 - \frac{T}{T_C}\right)$, where M_0 the saturation magnetization at 0 K is and T_C is the Curie temperature. Consequently, in the lowest order the magnetoabsorption must be proportional to $\left(1 - \frac{T}{T_C}\right)$ [41]. Fitting this dependence to the experimentally acquired data reveals that the Curie temperature of the studied spinel must be $T_C = 107$ K (see figure 7). This is in good agreement with the

expected Curie temperature of this compound estimated from the magnetometry measurements, showing that the magneto-absorption is a measure of the order parameter.

5. Time-resolved absorption spectroscopy

Figure 8 reveals the dynamics of the photo-induced absorption in the ferromagnetic spinel $Hg_{0.95}Cd_{0.05}Cr_2Se_4$. The measurements were performed with the pump and probe having the same central wavelength of 5.26 μm (matching the photon energy $\hbar\omega = 0.236$ eV of the pronounced peak). The magnetic field was applied in the sample plane in the horizontal direction. Each of the measured dependencies is characterized by a sharp increase of the signal during the temporal overlap of the pump and probe pulses, followed by a relaxation. In order to estimate the relaxation times, the signals were fitted using the function $f(t) = A_1 \cdot \exp\left(-\frac{t}{\tau_1}\right) + A_2$, where τ_1 is the relaxation time, and both A_1 and A_2 are amplitudes (see figure 9(a) and (b)). In a simple model of a two-level system, such behavior can be described in terms of excitation of the electrons into the excited state, followed by a relaxation. The characteristic time of the exponential decay τ_1 corresponds to the lifetime of the electrons in the excited state. The term A_2 represents laser-induced heating, which is often unavoidable in real experiments and relaxes on a time-scale much longer than 100 ps. It is seen that the signal is at its strongest at lower temperatures. Such an observation agrees with the absorption spectrum and, in particular, with the fact that the absorption peak at 0.236 eV increases in intensity upon decreasing the temperature. A noticeable decrease of the amplitudes A_1 and A_2 upon increasing the temperature from 7 K to 20 K can be attributed to the heating-induced change of the energy of the electronic transition. For example, a slight shift of the energy with respect to the spectrum of the laser pulse would lower the efficiency of the excitation and thus reduce the amplitudes of the photo-induced dynamics. After fitting the signals recorded when 7 K and 80 K, we deduce the relaxation time to be $\tau_1 = 3$ ps and $\tau_1 = 6$ ps respectively. Such an increase of the lifetime upon a decrease of the peak intensity is again in good qualitative agreement with the model of giant oscillator strength [17, 18].

6. Conclusions

Mid-infrared static and time-resolved spectroscopy of the ferromagnetic semiconductor $Hg_{0.95}Cd_{0.05}Cr_2Se_4$ was performed just below the absorption edge. It was shown that the absorption peak around 0.236 eV, which had been formerly related to intercenter transitions within the selenide vacancies and chromium complexes (ν_{Se}–Cr^{2+}), had significant dependence on temperature. Magnetoabsorption measurements showed a sensitivity of the energy of the transition to the magnetic order, suggesting that 3*d* electrons of Cr ions must play a decisive role in this transition. The lifetime of the electrons in the excited state was found to be in the range from 3 ps to 6 ps, and revealed a correlation with the oscillator strength of the transition. Such a correlation is in qualitative agreement with the behavior expected for weakly bound excitons. Therefore, in this ferromagnetic semiconductor, we discover an electronic excitation that has spectral features of a weakly bound exciton, coupled to the magnetic order.

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